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STUDIES ON THE PREPARATION OF
PYRIDINEMONOCARBOXYLIC ACIDS
BY CATALYTIC VAPOUR PHASE
OXIDATION OF ALKYL PYRIDINES

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BY CATALYTIC VAPOUR PHASE OXIDATION OF ALKYL PYRIDINES

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S. Järås and Sten T. Lundin

Submitted for publication

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S. Järås

Submitted for publication

Determination of Products Obtained by Catalytic Vapour Phase Oxidation of 2-Picoline, 3-Picoline and 2-Methyl-5-Ethylpyridine

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Summary

To prepare 2-pyridinecarboxylic acid (picolinic acid) and 3-pyridinecarboxylic acid (nicotinic acid), the vapour phase oxidation of a corresponding alkylpyridine is used. In order to analyse all the products of oxidation, a method with separate product condensation and formation of trimethylsilyl derivatives of the acids was developed. It has worked well during several years of use and is described in detail. Relative standard deviation for the analysis of 3-pyridinecarboxylic acid was 3.2%.

Introduction

The purpose of this investigation was to develop a quantitative method of analysis for the product stream from the vapour phase oxidation of 2-picoline, 3-picoline and 2-methyl-5-ethylpyridine respectively. The components of interest, besides the alkylpyridines, are the corresponding pyridinecarboxylic acids and pyridinealdehydes, pyridine, CO, CO₂, HCN, and maleic acid.

A method which has been used [1-3] is to condense the products and to analyse the pyridinecarboxylic acid by titrating with alkali and the other components mainly by gravimetric methods. This method fails when other acids, e.g. maleic acid, dissolved HCN and CO₂ are present. The acids can also be determined by polarographic methods [4-5]. The remaining non acidic liquid products, on oxidation of 3-picoline [5] have been estimated by gas chromatography.

By preparing the methyl- or ethylesters of 2-pyridinecarboxylic acid and 3-pyridinecarboxylic acid (picolinic acid and nicotinic acid respectively), these compounds can also be determined by gas chromatography [6]. A disadvantage of this method is that the esterification demands between 45 and 150 min [7]. This can be avoided by using the trimethylsilyl esters instead of the methyl- or ethylesters. In connection with the analysis of commercial multivitamin tablets, 3-pyridinecarboxylic acid has been estimated as the trimethylsilyl derivative prepared by the use of O,N-bis-(trimethylsilyl)-acetamide [8]. The accuracy of the method was not discussed however.

The analysis of 3-pyridinecarboxylic acid in different solutions was tested in our laboratory by gas chromatography. All columns tested adsorbed 3-pyridinecarboxylic acid very strongly. Not until the temperature was increased on a linear programme were peaks obtained, but with marked asymmetry and tailing. The same phenomenon has been observed by Ponomarev et al. [9]. With this in mind and considering that the tests with trimethylsilyl derivatives of the interesting acids gave good results, a method with condensation of the products and separate formation of derivatives of acids was developed. It has worked well during several years of use and is described in detail below.

This method will apply generally, not only to the preparation of 2- and 3-pyridinecarboxylic acids, as shown below, but also to 4-pyridinecarboxylic acid.

Method of Condensation and Separate Trimethylsilyl Derivative Formation of Acid

Apparatus

A Perkin Elmer F11 gas chromatograph with two flame ionization detectors was used. Column: 3.18 mm(1/8") steel X 1.5 m with 5% SE-30 on Chrom. W. 60/80 AW/DMCS. Carrier gas: nitrogen = 10 cm³/min (8.5 cm³/min for the products from 2-methyl-5-ethylpyridine oxidation); air = 230 cm³/min; hydrogen = 30 cm³/min. Column temperature: 70 °C for analysis of the chloroform phase and 130 °C for analysis of the acid derivatives. Corresponding injection temperatures: 115 °C and 175 °C.

Reagents

Chloroform, 2-picoline, chlorobenzene, 1,2,4-trichlorobenzene and N,O-bis-(trimethylsilyl)-acetamide were all "pro analysi". The solution of chloroform used for extraction contained 2 vol percent chlorobenzene as internal standard in the oxidation of 2-picoline and 2 vol percent 2-picoline in the oxidation of 3-picoline and 2-methyl-5-ethylpyridine. The pyridine for dissolving the acids contained 7 vol percent 1,2,4-trichlorobenzene as internal standard.

Procedure

The reactants, alkylpyridine and air, are passed through a reactor, filled with catalyst, followed by a condensing system. The condensing system consists of first 3 U-tubes,

then 4 bubblers containing water and finally 2 tubes with glass wool. The first U-tube is kept at -20°C and the last two at -50°C and -60°C by means of freezing mixtures. The gas from the last tube with glass wool is then passed through ascarite and bubblers with concentrated sulphuric acid in which water and nitrogen oxides are absorbed. The amount of CO_2 in the issuing gas is determined gravimetrically by means of ascarite-dehydrite. The CO is converted at 130°C to CO_2 by means of iodine pentoxide and the resultant CO_2 is absorbed in ascarite-dehydrite. HCN is determined by letting a part of the product gas pass over a salt of mercury, where it is converted to an acid which colours a calibrated indicator red.

The total amount of the alkylpyridine passed through the reactor is about 0.2–0.4 g. Immediately after the reactant stream through the reactor is ended, a nitrogen stream of $150\text{ cm}^3/\text{min}$ is passed through the condensing system for 15 min in order to carry all the CO_2 to the ascarite-dehydrite. The condensed products are then extracted twice by means of a chloroform-water mixture beginning with the last tube containing glass wool. The total volume after extraction amounts to 10 cm^3 chloroform solution and 20 cm^3 water including the water in the bubblers. The acid is not dissolved in the chloroform but is found in the aqueous phase.

In the quantitative estimations by gas chromatography below, the method with internal standardization is used. Known weight ratios of the sample relative to the standard are prepared and chromatographed. Peak areas are estimated by multiplying the peak height by the width at half-height and area ratios are plotted against weight ratios. In the unknown area ratios are measured and the weight ratio of the unknown to the standard is obtained from the calibration curve.

In order to analyse the nonacidic components, 1.0 mm^3 of the chloroform phase is injected into the gas chromatograph. The column separates incoming alkylpyridine and any other alkylpyridines, pyridine and pyridinealdehydes formed (see Tables I–III).

The aqueous phase is diluted to 100 cm^3 . From this $5\text{--}15\text{ cm}^3$ is evaporated at 45°C and the residue obtained dissolved in 1.0 cm^3 pyridine solution and

Table I. Retention times for products from oxidation of 2-picoline. Injection 1.0 mm^3 , column: 3.18 mm ($1/8''$) steel $\times 1.5\text{ m}$ with 5 % SE-30 on Chrom. W. 60/80 AW/DMCS, column temperature: 70°C , carrier gas: nitrogen = $10\text{ cm}^3/\text{min}$, FID.

Product	Retention time min
chloroform	0.5
pyridine	2.0
2-picoline	3.3
chlorobenzene (internal standard)	4.5
2-pyridinealdehyde	9.0

Table II. Retention times for products from oxidation of 3-picoline. Injection 1.0 mm^3 , column 3.18 mm ($1/8''$) steel $\times 1.5\text{ m}$ with 5 % SE-30 on Chrom. W. 60/80 AW/DMCS, column temperature: 70°C , carrier gas: nitrogen = $10\text{ cm}^3/\text{min}$, FID

Product	Retention time min
chloroform	0.5
pyridine	2.0
2-picoline (internal standard)	3.3
3-picoline	4.8
3-pyridinealdehyde	10.0

Table III. Retention times for products from oxidation of 2-methyl-5-ethylpyridine. Injection 1.0 mm^3 , column: 3.18 mm ($1/8''$) steel $\times 1.5\text{ m}$ with 5 % SE-30 on Chrom. W. 60/80 AW/DMCS, column temperature: 70°C , carrier gas: nitrogen = $8.5\text{ cm}^3/\text{min}$, FID

Product	Retention time min
chloroform	0.5
pyridine	2.2
2-picoline (internal standard)	4.0
3-ethylpyridine	11.5
3-vinylpyridine	13.0
3-pyridinealdehyde	15.0
2-methyl-5-ethylpyridine	19.5
2-methyl-5-vinylpyridine	21.0
5-ethyl-2-pyridinealdehyde	55.0

0.5 cm^3 of N,O-bis-(trimethylsilyl)-acetamide added. The solution is then heated at 70°C for 5 min and the resulting trimethylsilyl derivative determined by gas chromatography (see Fig. 1). The trimethylsilyl derivative of maleic acid is obtained as a separate peak immediately after that of 3-pyridinecarboxylic acid (not shown in Fig. 1). The 2-pyridinecarboxylic acid derivative has about the same retention time as the derivative of 3-pyridinecarboxylic acid.

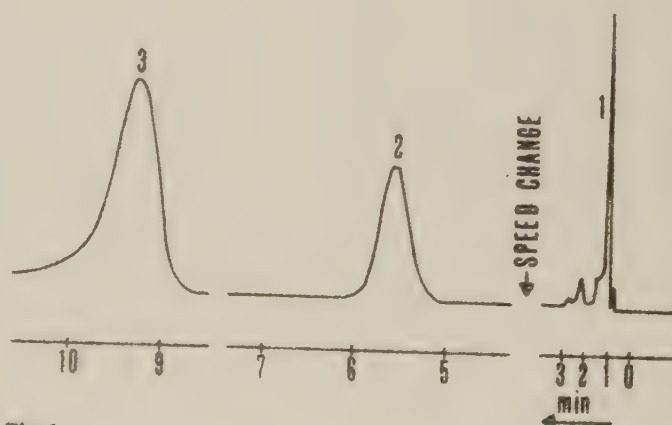


Fig. 1

- Trimethylsilyl derivative of 3-pyridinecarboxylic acid. Injection 1.0 mm^3 , column: 3.18 mm ($1/8''$) steel $\times 1.5\text{ m}$ with 5 % SE-30 on Chrom. W. 60/80 AW/DMCS, column temperature: 130°C , carrier gas: nitrogen = $10\text{ cm}^3/\text{min}$, FID
- (1) pyridine and N,O-bis-(trimethylsilyl)-acetamide
- (2) 1,2,4-trichlorobenzene (internal standard)
- (3) trimethylsilyl derivative of 3-pyridinecarboxylic acid

The trimethylsilylacetamide is decomposed giving a small white coating of SiO_2 on the collector assembly of the FID. This causes the sensitivity to decrease. Therefore two injections should always be made and the collector assembly washed with water and acetone and dried before the first injection. The amount of 3-pyridinecarboxylic acid is calculated from the average of the first and the second injection. The accuracy of the method in determining 3-pyridinecarboxylic acid has been estimated in the following way. 10.53 mg 3-pyridinecarboxylic acid was accurately weighed and determined by the above method from 5 determinations to be 10.68 ± 0.34 mg (see Table IV). This corresponds to a relative standard deviation of $\pm 3.2\%$.

Table IV. Determination of 3-pyridinecarboxylic acid as a trimethylsilyl derivative by gas chromatography. 10.53 mg 3-pyridinecarboxylic acid was accurately weighed and determined by the recommended method

Experiment number	Weight determined mg
1	10.40
2	11.10
3	11.00
4	10.50
5	10.40

Conclusions

To analyse products from oxidation of alkylpyridine, a method using condensation followed by extraction of the products with a mixture of chloroform-water is recommended. The method involving the preparation of trimethylsilyl derivatives of the acids is especially recommended. The method has been applied for several years and works well.

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PREPARATION OF PYRIDINEMONOCARBOXYLIC ACIDS BY CATALYTIC
VAPOUR PHASE OXIDATION OF ALKYL PYRIDINES

Part I. Oxidation of 2- and 3-picoline - and decarboxylation
of 2- and 3-pyridinecarboxylic acid in the vapour phase

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Synopsis

The vapour phase oxidation of 2-picoline with air using a singly promoted vanadium catalyst (V_2O_5/SnO_2 , mole ratio 1/1.5), at a temperature of $375^\circ C$ and a space velocity of $6130\ h^{-1}$, gave a 69% conversion with a selectivity of 64% for 2-pyridinealdehyde. No pyridoin formation was detected. In the vapour phase oxidation of 3-picoline using a doubly promoted vanadium catalyst ($V_2O_5-TiO_2-Na_2O$ with $V/Ti/Na = 100/20/1.15$) at a temperature of $400^\circ C$ and a space velocity of $1450\ h^{-1}$, a 94% conversion of 3-picoline was obtained with a selectivity of 51% for niacin (3-pyridinecarboxylic acid) and 1% for 3-pyridinealdehyde. By varying the atom ratio V/Ti , the catalyst $V/Ti = 100/25$ was found to be the most active one. The decarboxylation of 2- and 3-pyridinecarboxylic acid in the vapour phase was also investigated under the conditions used in the oxidation of the picolines to the acids. At $350^\circ C$ about 90% decarboxylation of picolinic acid occurs under these conditions, while only a few per cent of the niacin decarboxylated to pyridine between 300 and $500^\circ C$.

1. Introduction

2-Pyridinecarboxylic acid (picolinic acid) and 3-pyridinecarboxylic acid (nicotinic acid or niacin) are technically valuable products. For example, a derivative of picolinic acid can be used as a local anaesthetic¹ (Carbocain or Scandicain). Niacin is an important vitamin of the B-complex and so is its amide. Many drugs²⁻³ based on niacin have curative effects such as: lowering the level of cholesterol and free fatty acids in the blood, stimulation of the respiratory apparatus, anti-spasmodic and antirheumatic action etc.

On a large scale the acids are prepared by oxidizing a corresponding alkylpyridine in the liquid phase. Picolinic acid is prepared from 2-picoline with potassium permanganate as an oxidizing agent. Niacin is prepared from 3-picoline or 2-methyl-5-ethylpyridine (MEP) in the liquid phase at high pressure with nitric acid as an oxidizing agent. If air could instead be used as oxidizing agent, and high enough yields could be obtained, the cost would be lowered and the technique of production simplified. Attempts have been made to oxidize 2-picoline⁴⁻⁶ and 3-picoline⁶⁻¹¹ in the vapour phase to the corresponding pyridinecarboxylic acid using air as the oxidizing agent. The present investigations were undertaken in order to study the catalytic vapour phase oxidation of 2- and 3-picoline, bearing in mind the possibility of developing industrial methods for the production of picolinic acid and niacin.

It is known that carboxylic acids decarboxylate on heating¹². Decarboxylation of picolinic acid in the molten state¹³ and in

solvents¹⁴⁻¹⁵ has been reported previously, but not in the vapour phase. Only the thermal decarboxylation of some salts of niacin has been investigated¹⁶ earlier. The decarboxylation of picolinic acid and niacin in the vapour phase is studied below.

2-Pyridinealdehyde is easily oxidized by air in the liquid phase¹⁷. With this in mind, and considering that a substantial decarboxylation of picolinic acid is obtained in the vapour phase oxidation of 2-picoline, another way to prepare picolinic acid is suggested: first to oxidize 2-picoline to the 2-pyridinealdehyde in the vapour phase by air, and then in a second step to oxidize the aldehyde to picolinic acid in the liquid phase. Attempts with vapour phase oxidation of 2-picoline to 2-pyridinealdehyde have been reported for a number of catalysts^{9,18-20}.

Vapour phase oxidation of 3-picoline over a titanium vanadate catalyst has been reported previously¹⁰. In earlier work in our laboratory on the oxidation of o-xylene to phthalic anhydride²¹, the promotor effect of titanium dioxide was investigated, giving the results that the atom ratio V/Ti = 100/20 appeared to be most favourable. Consequently in this work we have studied the effect of the addition of varying amounts of titanium dioxide as promotor to vanadium pentoxide.

In the preparation of phthalic anhydride²², a double promotor additive with titanium dioxide as well as alkali oxides, especially potassium oxide, appeared to have a good influence, as it increased the desired yields and decreased the total oxidation. The results of tests using these additives in the oxidation of 3-picoline are also presented below.

2. Experimental

2.1 Apparatus and procedure

A schematic diagram of the apparatus used is illustrated in fig. 1. The apparatus included four main units: a feeding system for introducing controlled amounts of alkylpyridine, air and steam; the catalytic reactor; a product recovery unit; and an analysis unit including a total oxidation reactor.

In the experiments, primary air was passed through the thermostated vaporizer with alkylpyridine. The resultant gas stream was mixed with secondary air and steam to the desired composition. The percentage of alkylpyridine in the reactant stream was determined by oxidizing the alkylpyridine totally to carbon dioxide, water and nitrogen oxides, and analysing the percentage of carbon dioxide by gas chromatography.

The reactant stream was preheated and passed through the fixed bed reactor filled with the catalyst studied. The reactor was made of glass tubing, 14 mm in internal diameter and 300 mm long. After about one hour's run with constant experimental conditions, steady conditions were obtained. The product recovery from the reactant stream was then started. When a total of 0.2 - 0.4 g of the products had been obtained, the experimental conditions were adjusted to new values, normally a new temperature.

2.2 Analytical

The products emerging from the reactor were passed through a condensing and absorption system. This system consisted of first 3 U-tubes, then 4 bubblers containing water, and finally

2 tubes with glass wool. The first U-tube was kept at -20°C and the last two at -50°C and -60°C , respectively.

The carbon dioxide was absorbed in an ascarite-dehydrite-tube. The carbon monoxide was oxidized further to carbon dioxide, and was then determined using another ascarite-dehydrite-tube. The hydrogen cyanide was determined by allowing part of the product gas to pass through a DRÄGER tube (Drägerwerk, Lübeck, W. Germany). After the completion of the experiment, the condensed products were extracted twice by means of a chloroform-water mixture, beginning with the last tube containing glass wool. The total volume after extraction amounted to 10 ml of chloroform solution and 20 ml of water, including the water in the bubblers. The acid was not dissolved in the chloroform, but was found in the aqueous phase.

The percentage of the products in the chloroform phase (incoming alkylpyridine, pyridine and pyridinealdehydes formed) were determined by gas chromatography (column; 5% SE-30 at 70°C). The percentage of picolinic acid was determined in early experiments by titrating the aqueous phase with alkali, a method which however resulted in too high values, because alkali is also consumed by formed and dissolved carbon dioxide, hydrogen cyanide etc. This method was later replaced by a gas chromatographic method, using a trimethylsilyl derivative, which was more reliable (for further details, see Järås²³).

2.3 Materials

2- and 3-picoline, picolinic acid and niacin were of chromatographic purity. The chemicals used for catalyst preparation below were of laboratory reagent purity.

2.4 Catalysts

1. Tin vanadate catalyst, V_2O_5/SnO_2 , precipitated and sintered:

The catalyst was prepared according to Lewis and Brown⁵.

These authors, on oxidation of 2-picoline, claimed a selectivity of 18.8% for picolinic acid, determined by titrating with alkali. This is the highest yield of picolinic acid reported prior to the present work. The specific area was determined to be $S_A = 0.5 \text{ m}^2/\text{g}$ by the BET-method²⁴.

2. A vanadium catalyst, $V_2O_5/KHSO_4$, on silica gel as a carrier:

The catalyst was prepared according to a Ciba patent²⁵, which reports yields of 62% niacin on oxidation of 2-methyl-5-ethylpyridine. This seems to be the highest yield of niacin ever obtained from 2-methyl-5-ethylpyridine. (Silica gel $S_A = 673 \text{ m}^2/\text{g}$).

3. Tin vanadate catalyst, $V_2O_5/SnO_2 = 1/1.5$: The catalyst was prepared according to Chekmareva²⁶, who reports a yield of 75% on oxidation of quinoline to niacin. This is the highest yield of niacin from quinoline previously reported. ($S_A = 0.5 \text{ m}^2/\text{g}$).

4-13. The melted vanadium catalysts numbered 4-13 were prepared by mechanical mixing of the components in charges of about 150-200 g filled in a crucible (150 cm^3) with cover and heated in a tube oven at 1250°C for 3 hours. The crucible was then removed from the oven and allowed to cool to room temperature. After cooling in the crucible, the catalyst was crushed and sifted to obtain the desired size.

In addition to vanadium pentoxide, the components were as follows: titanium dioxide, tin dioxide, potassium carbonate, sodium carbonate and calcium carbonate (in separate experiments). The atom ratios for the different catalyst component mixtures are shown in table 2.

The specific area for these molten catalysts was low ($0.2 - 1.0 \text{ m}^2/\text{g}$), with no significant trend.

10. According to a German patent²⁷, a $\text{V}_2\text{O}_5\text{-TiO}_2$ catalyst on a carrier gave a good yield in a preparation of phthalic anhydride. With pumice stone as a carrier, the catalyst was prepared according to this patent. The atom ratio V/Ti was 23.5/100.

The particle size of the catalysts was 14 - 25 mesh.

3. Results and discussion.

3.1 Oxidation of 2-picoline to picolinic acid

With the four catalysts 1 - 4 and 12, the oxidation of 2-picoline with air in the absence of additives produced 2-pyridine-aldehyde, piculinic acid, pyridine, carbon dioxide, carbon monoxide, water and small amounts of pyridine and hydrogen cyanide. The percentage of picolinic acid was low at all temperatures, one to a few per cent. With increasing temperatures, the percentage of pyridine passed first through a maximum, and then the percentage of carbon dioxide rapidly increased. The low yield of picolinic acid was therefore probably due to decarboxylation of most of the primarily formed picolinic acid

to pyridine, with the result that the maximum yield of picolinic acid only reached a few per cent.

The addition of steam had a mixed effect, partly through a substantial increase in the oxidation speed, and partly by increasing the percentage of 2-pyridinecarboxylic. The yield of picolinic acid was however invariably low.

The addition of ethanol or formic acid²⁸ in the vapour phase as decarboxylation inhibitors, gave small positive effects at low temperatures (210 - 250°C), but failed at higher temperatures due to destruction by oxidation. For all catalysts tested, the yield of picolinic acid was, with or without additives, very low and quite insufficient for technical purposes. The highest yield, 4%, was obtained for catalysts 12 and 3 at 375°C, 0.56% 2-pyridine in the feed, and space velocity 5520 h⁻¹.

3.2 The decarboxylation of picolinic acid

A separate investigation of the decarboxylation reaction of picolinic acid in the vapour phase was carried out in order to verify the above suggestion that the decarboxylation resulted in the very low yields of picolinic acid obtained.

The decarboxylation was measured at different temperatures for a mixture of picolinic acid and air. Experiments were carried out with and without catalysts, at varying space velocities and in the presence or absence of steam. The degree of decarboxylation was determined by estimating the amount of picolinic acid in the gas mixture before and after the reaction. The results are given in fig. 2.

We found that picolinic acid begins to decarboxylate in the vapour phase at about 200°C . At space velocities of $4600 - 12\,300\text{ h}^{-1}$, equivalent to the conditions of oxidation experiments and without catalyst present, the decarboxylation was complete at $350 - 400^{\circ}\text{C}$.

The decarboxylation was found to be an irreversible reaction of first order. The activation energy for decarboxylation in the vapour phase was estimated from experimental data at $270 - 320^{\circ}\text{C}$ to be 98 kJ/mole . Clark¹³ reports the activation energy for decarboxylation in the molten state to be 167 kJ/mole .

In the presence of catalyst No 3, the extent of decarboxylation was increased at lower temperatures, but at higher temperatures the extent of decarboxylation was the same as in an empty reactor. The addition of steam increased the decarboxylation only at lower temperatures.

Substantial decarboxylation of picolinic acid was thus obtained in the temperature interval in which the 2-picoline was oxidized and the picolinic acid was formed. Furthermore, the decarboxylation was primarily dependent on the thermal instability of picolinic acid. The catalyst and its surface played only a minor role in this connection. The possibility of reducing the decarboxylation in a catalytic way through the use of inhibitors could therefore not be regarded as plausible. More promising was the possibility of reducing the losses by carrying out the oxidation on the aldehyde instead.

3.3 Oxidation of 2-picoline to 2-pyridinealdehyde

Variation of the percentage of 2-picoline and of the space velocity led to the determination of the following suitable test conditions: a concentration of 2-picoline of 0.56 mole-% and a space velocity around 4800^{-1} without steam additive. The catalyst bed volume was 6 cm^3 and the length 26 mm. The temperature was varied within the interval $250 - 500^{\circ}\text{C}$, at which the percentage of 2-pyridinealdehyde passed through a maximum. The maximum yields obtained for 2-pyridinealdehyde at a single pass over the four catalysts examined are shown in table 1, together with the associated values of conversion and selectivity.

Sintered or partially melted catalysts with a small specific area were more favourable from the point of view of yield and selectivity than precipitated catalysts with high specific area and fine pores.

Without addition of steam low yields of the aldehyde were obtained, partly as a consequence of the further oxidation to picolinic acid which was then decarboxylated, and partly as a consequence of complete total oxidation. As can be seen from the data of catalyst No 3, the addition of steam caused a substantial increase in the maximum yield of aldehyde as a consequence of higher selectivity at higher conversion.

At this maximum, 64% of the converted 2-picoline was thus oxidized to 2-pyridinealdehyde, 32% was recovered as pyridine obtained through decarboxylation of picolinic acid, and 5% was completely oxidized to carbon dioxide and water. The percentage

yield of picolinic acid was lower than 0.5%. With this catalyst and steam additive no pyridoin was obtained either.

At higher temperatures, a substantial oxidation of the pyridine ring to carbon dioxide and hydrogen cyanide was obtained. At 475°C , a previously undetected substance was found: namely about 2% of 2-picolinenitrile.

In the study of the time necessary to reach a stationary state for catalyst No 3, a stationary state was obtained after 30 min, after which the same product distribution was obtained for the prolonged measurements during the 6.5 hours of the experiment.

The variation of the temperature in the catalyst bed with the normal reactor and usual catalyst bed (6 cm^3) was found to be 4° at 400°C .

In order to determine whether the pyridinealdehyde could also be oxidized to picolinic acid in the vapour phase without catalyst, the space after the catalyst bed was lengthened and held at reaction temperature so that the space velocity was changed from 6130 h^{-1} to 1380 h^{-1} . No further oxidation of the aldehyde could be detected.

3.4 The decarboxylation of niacin

In view of the experience with the decarboxylation in the preparation of picolinic acid, the thermal decarboxylation of niacin in the vapour phase was also investigated under the conditions used in the oxidation of 3-picoline using the same method as described for picolinic acid.

The results are given in fig. 3. A considerably higher temperature, about 300°C higher, was required for the decarboxylation of niacin compared to that of picolinic acid. Thus, a temperature of 600°C was required for a 20% decarboxylation at a space velocity of 2600 h^{-1} .

The decarboxylation reaction was found to be irreversible and of first order. The activation energy was calculated from the experimental rate data at $600 - 700^{\circ}\text{C}$ to be 220 kJ/mole .

At the space velocities and the temperatures ($300 - 500^{\circ}\text{C}$) used for the oxidation of 3-picoline to niacin, only a few per cent of niacin decarboxylates to pyridine.

3.5 Oxidation of 3-picoline to niacin and 3-pyridinealdehyde

The oxidation of 3-picoline by air in the vapour phase over vanadium catalysts gave the following products: 3-pyridinealdehyde, niacin, pyridine, carbon dioxide, carbon monoxide, water and small amounts of hydrogen cyanide, with different product distributions at different temperatures. At lower temperatures, niacin and 3-pyridinealdehyde were predominant as products, and in both cases the yields passed through maxima. The maximum of niacin was obtained at a higher temperature than that of the aldehyde, and the yields of niacin were always considerably higher than those of the aldehyde. The percentage of pyridine was constantly low. The amount of carbon oxides formed by total oxidation increased monotonously with increasing temperature.

On the basis of the results from the 2-picoline oxidation above, a vanadium-tin catalyst ($\text{V}_2\text{O}_5/\text{SnO}_2 = 1/1.5$) was chosen in order

to determine suitable conditions with respect to space velocity and mole ratios of oxygen/3-picoline and steam/3-picoline for the subsequent tests of different catalysts.

This led to the following test conditions: space velocity 2600 h^{-1} , mole ratio oxygen/3-picoline = 42 and mole ratio steam/3-picoline = 82. The catalyst bed volume was 13.5 cm^3 and the length was 60 mm. With these parameters fixed, the conversion and product distribution were investigated for each catalyst as functions of the temperature. Normally, experiments were carried out for each catalyst, at five to seven different temperatures separated by about 25°C each, in order to cover the interesting temperature range with maxima for 3-pyridinealdehyde as well as for niacin.

The stability of the catalyst under the typical process conditions was examined using catalysts 1 and 5, respectively, for a period of seven hours. The activity of the catalysts was found to remain fairly constant, after 30 minutes, during this period. The variation of the temperature in the catalyst bed was found to be 12° at 400°C .

In figure 4, as an example, data are shown for the oxidation of 3-picoline over catalyst No 6. The mole percentage of unconverted 3-picoline and the conversion to the different products, calculated per mole of 3-picoline in the feed, are represented as functions of temperature.

In table 2, the maximum yields obtained and the selectivities for the different catalysts under the fixed test conditions

are shown. Besides the values for niacin, the values for the sum of niacin and 3-pyridinealdehyde are also shown, as the pyridinealdehyde can easily be oxidized in the liquid phase to the acid¹⁷.

The maximum conversions to the sum of niacin and aldehyde presented in the table reflect the possibilities to make use of the most ideal process design, in which all or practically all incoming 3-picoline is converted, so that no separation or recirculation of unconverted 3-picoline is required. The maximum selectivity values presented in the table reflect the maximum yields which can be obtained on separation and recirculation of unconverted 3-picoline.

As far as can be judged from the present results, it does not seem to be possible to combine the stipulation of a high yield of niacin, or niacin plus aldehyde, with that of complete conversion of 3-picoline. It is clear from the table that the best values obtained for maximum conversion to niacin plus 3-pyridinealdehyde are at about 40%. The following catalysts are then about equivalent from the viewpoint of yield: unpromoted vanadium oxide (No 4), vanadium tin oxide catalyst (No 3) and vanadium titanium oxide catalyst with the atom ratio V/Ti = 100/25 (No 7). If for these catalysts the conversion of 3-picoline is increased further by for example increasing the oxidation temperature, the conversion to niacin and 3-pyridinealdehyde decreases markedly.

The difficulty of combining high yields with a complete conversion of 3-picoline is due to the higher predominance of total oxidation at an increased extent of conversion, which seems to apply to all the catalysts. The decarboxylation of niacin to pyridine plays only a secondary role.

The anticipated positive effect of the alkali promotor analogues on the oxidation of o-xylene failed to appear. The reason for this is not yet known. One possible explanation is that the addition of steam blocks or neutralises this favourable effect, as the oxidation of o-xylene was carried out in the absence of steam.

In order to minimize the consumption of the alkylpyridine it is most favourable to choose process conditions corresponding to the maximum of selectivity for niacin plus aldehyde, which in this case gives the net yield at separation and complete recirculation of unconverted 3-picoline. As can be seen from table 2, substantially higher values are obtained. The best value, 85%, is obtained for unpromoted vanadium oxide (No 4). The second best value, 82%, is obtained for vanadium-titanium oxide catalyst with the atom ratio $V/Ti = 100/20$ (No 6). These best net yields are obtained at a conversion of about 40%, corresponding to a recirculation ratio of 1.5/1.

The results presented above regarding maximum conversions, yields and selectivities were obtained under the same test conditions for all catalysts and thus do not necessarily correspond to the optimum conditions for the individual catalysts.

3.6 Effect of changing the space velocity for one catalyst

Catalyst No 12 (V/Ti/Na = 100/20/1.15) gave the most pure product and at the same time good yields compared to the other catalysts. In order to determine the effect of space velocity, experiments were carried out on nine different levels at 400°C for this catalyst. The maximum yield was obtained at the space velocity 1450 h⁻¹, giving 48% niacin and 1% aldehyde at a 94% conversion of 3-picoline. The maximum yield of niacin plus aldehyde could thus be increased from 31% under the test conditions to 49% by lowering the space velocity in this case.

3.7 Comparison between V₂O₅-TiO₂-catalysts with different V/Ti ratios

The choice of a catalyst for a large scale operation is not only dependent on the yield conditions but also to a large extent on the following two factors: 1) the activity of the catalyst and 2) the quality and purity of the product obtained.

Promotion of vanadium oxide with titanium oxide influences the activity as well as the yield conditions. Fig 5 A shows the conversions to niacin and 3-pyridinealdehyde and unconverted 3-picoline at 375°C as functions of the atom ratio V/Ti. The best yield of niacin and the greatest conversion of 3-picoline at 375°C are obtained for the promotor ratio V/Ti = 100/25.

In fig 5 B the maximum yields of niacin with the corresponding yields of 3-pyridinealdehyde and the temperature at this maximum are shown as functions of the atom ratio V/Ti. Here it also appears that the catalyst with V/Ti = 100/25 is most active. The maximum conversion to niacin as well as to the sum of niacin

and aldehyde is indeed the same as for the unpromoted vanadium oxide, but the maximum is obtained at 365°C instead of 440°C, i.e. at considerably lower temperature.

By promoting with TiO_2 a valuable increase in the catalyst activity was obtained without decreasing the maximum conversion to niacin at a single pass in the reactor. This increase in activity was furthermore obtained with no substantial decrease in selectivity.

Acknowledgements

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Appendix

Definitions

- conversion = the mole percentage of the limiting reactant in the reactor feed that is converted and disappears
- selectivity = the quantity of the limiting reactant that goes to form the desired product in the reactor effluent, expressed as a mole percentage of the total quantity of the limiting reactant that is converted
- space velocity = the gaseous volume at 25°C and atmosphere pressure of the total feed per hour per unit volume of catalyst bed
- yield = conversion x selectivity

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Figure 1

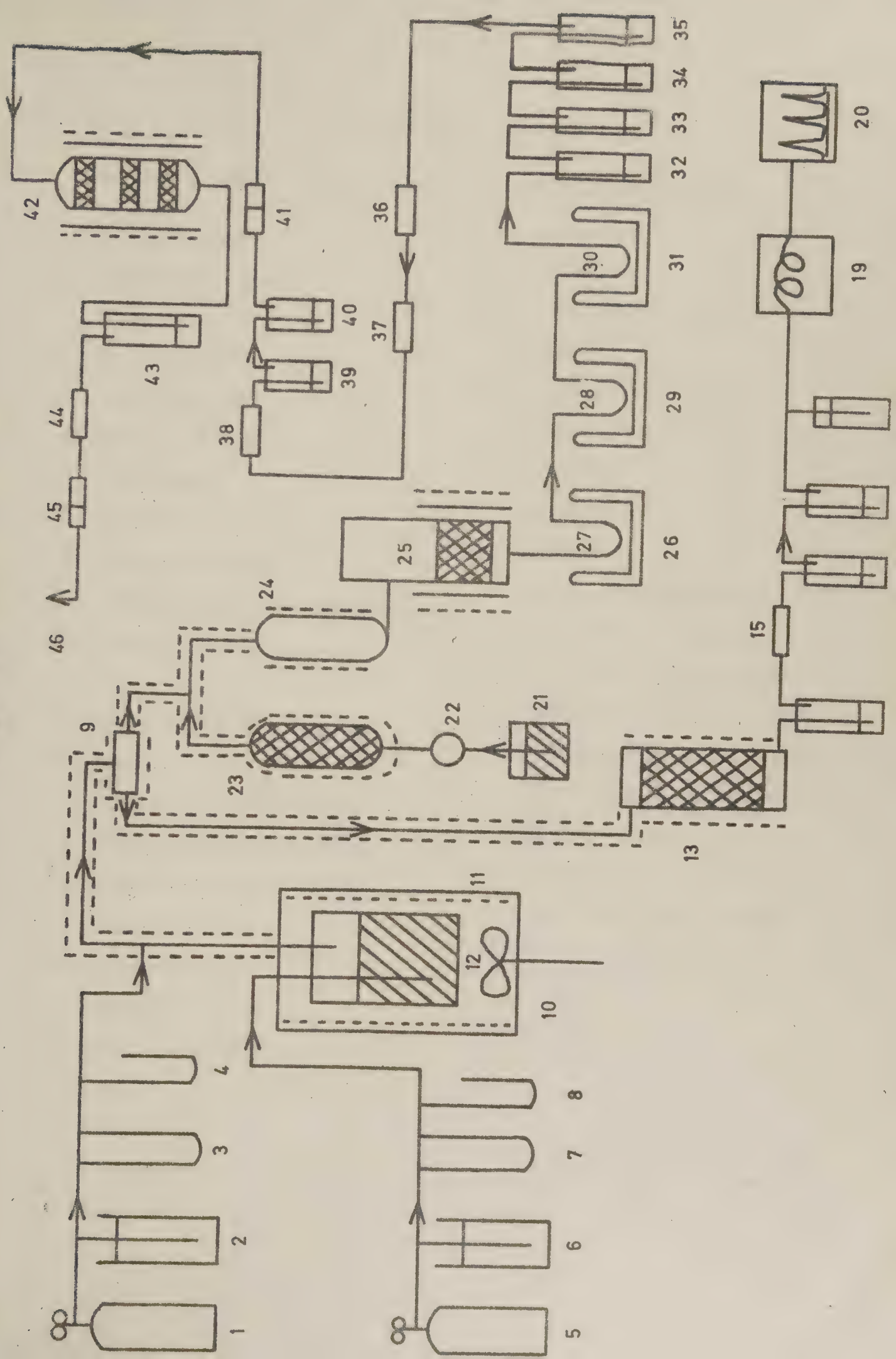


Figure 1

Schematic diagram of apparatus

1. Air cylinder
2. Bleed-off-tube
3. Flow meter
4. Pressure meter
5. Air cylinder
6. Bleed-off-tube
7. Flow meter
8. Pressure meter
9. Three way valve
10. Alkylpyridine evaporator
11. Heating mantle
12. Fan
13. Total oxidation reactor
14. Bubbler
15. Tube with drying agent
16. Bubbler with conc. H_2SO_4
17. Bubbler with conc. H_2SO_4
18. Bleed-off-tube
19. Chromatograph
20. Recorder
21. Water reservoir
22. Pump
23. Evaporator
24. Preheater
25. Reactor

26. Insulating bottle
 27. U-tube
 28. U-tube
 29. Insulating bottle
 30. U-tube
 31. Insulating bottle
 32. Bubbler
 33. Bubbler
 34. Bubbler
 35. Bubbler
 36. Tube with glasswool
 37. Tube with glasswool
 38. Tube with drying agent
 39. Bubbler with conc. H_2SO_4
 40. Bubbler with conc. H_2SO_4
 41. Tube with ascarite-dehydrite
 42. Reactor with I_2O_5
 43. Bubbler
 44. Tube with drying agent
 45. Tube with ascarite-dehydrite
 46. Outlet
- === Heated parts

Bubblers No 16-17 and 39-40 are used to adsorb nitrogen oxides.

Figure 2

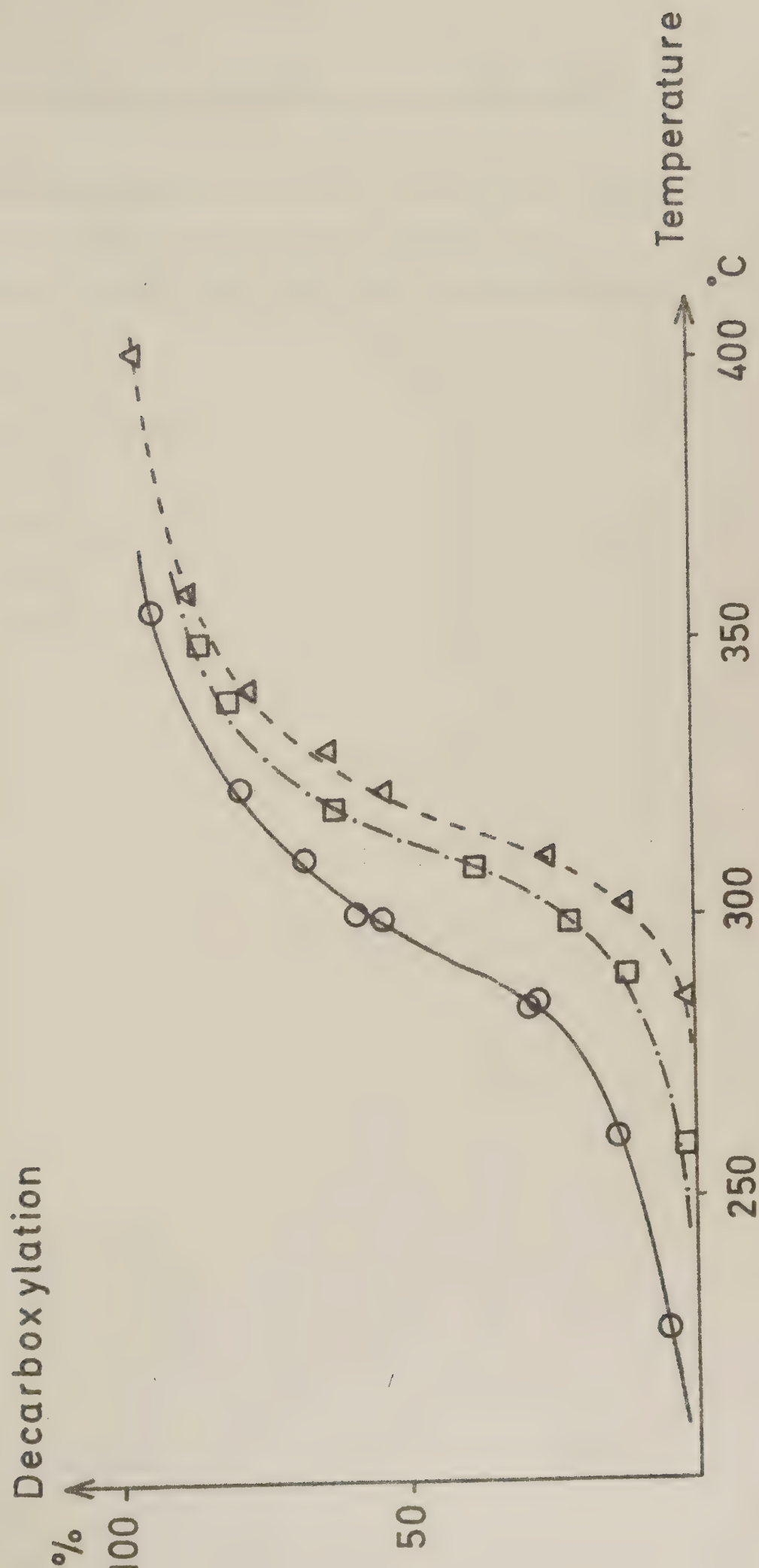


Figure 2. Vapour phase decarboxylation of picolinic acid

Vapour phase decarboxylation of picolinic acid in air in an empty reactor at three different space velocities as a function of reactor temperature. Mole ratio: oxygen/picolinic acid = 900.

	Space velocity h^{-1}
— — — — —	12 300
— . — . — .	6 100
—————	4 600



Table 1. Catalytic vapour phase oxidation of 2-picoline

Maximum yields for 2-pyridinealdehyde at a single pass and associated values of conversion and selectivity (mole ratio oxygen/2-picoline was 37).

	Yield g *	Conversion g *	Selectivity g *	Temp °C	Space velocity h ⁻¹	H ₂ O/2-picoline mole ratio
1. Tin vanadate catalyst V ₂ O ₅ /SnO ₂ , precipitated	3	55	6	260	5300	-
2. V ₂ O ₅ /KHSO ₄ on silica gel as carrier	1	27	4	435	4210	-
12. V ₂ O ₅ /TiO ₂ /Na ₂ O, melted (V/Ti/Na = 100/20/1.15)	11	43	25	365	4800	-
3. V ₂ O ₅ /SnO ₂ = 1/1.5, melted	12	35	33	375	4470	-
3. - " -	44	69	64	375	6130	82

* Mole per cent

Figure 3

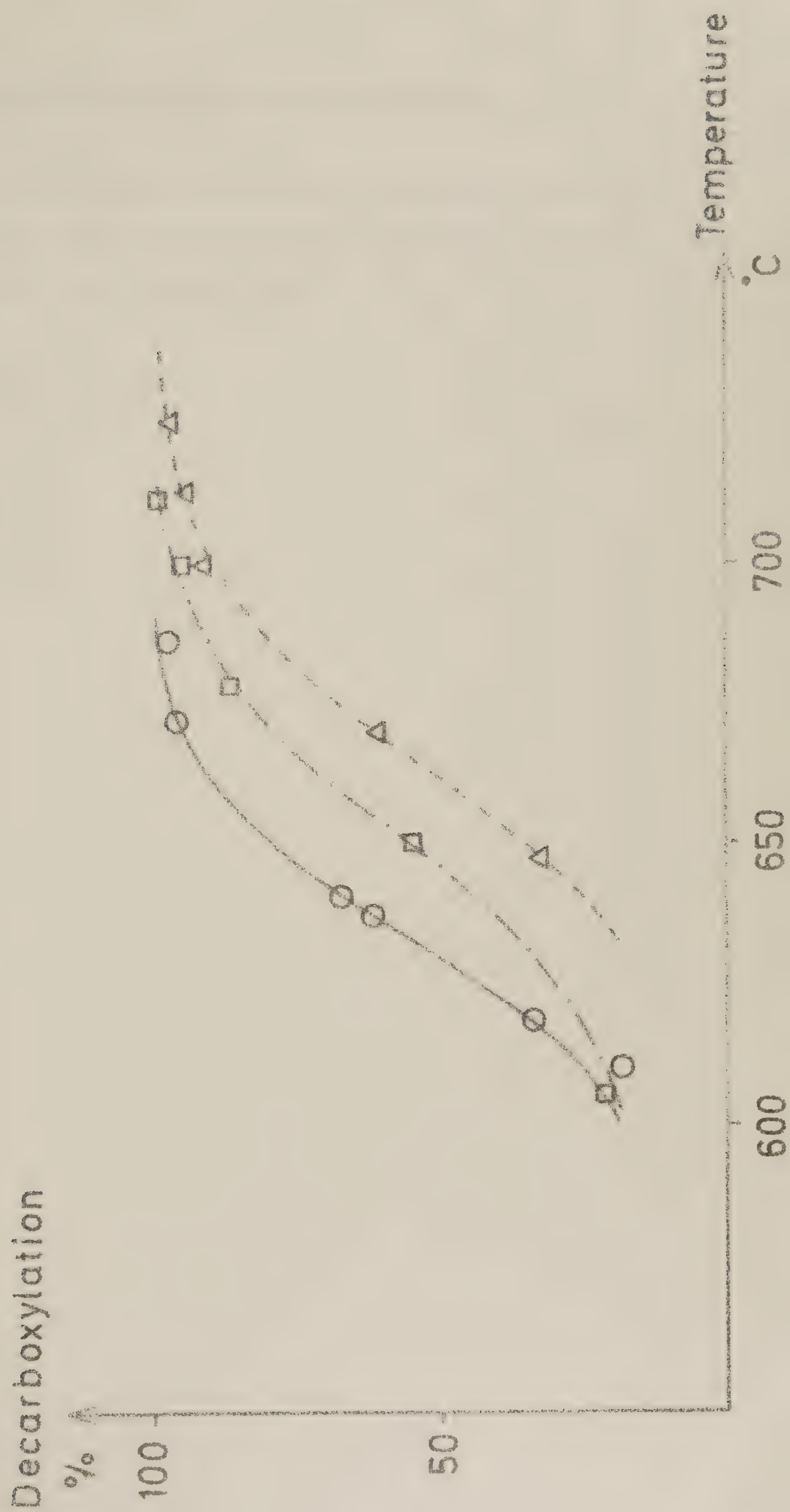


Figure 3. Vapour phase decarboxylation of niacin

Vapour phase decarboxylation of niacin in an empty reactor at three different space velocities as functions of reactor temperature. Mole ratio: Oxygen/niacin = 145.

Space velocity	
jh^{-1}	
— — — — —	4110
— • — • — •	2115
—————	1130

Figure 4

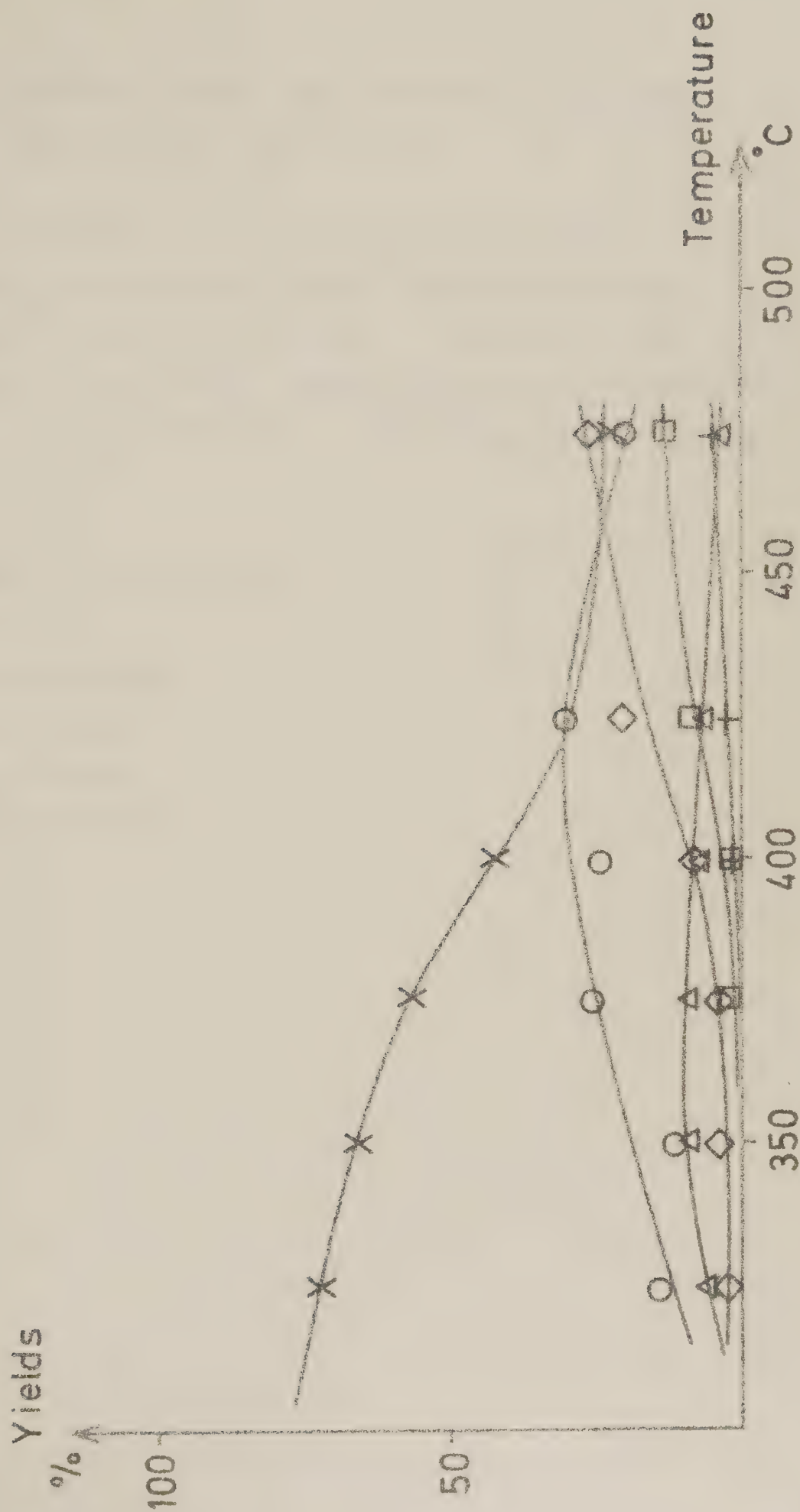


Figure 4. Catalytic vapour phase oxidation of 3-picoline
over catalyst V/Ti = 100/20

The mole percentage of unconverted 3-picoline and the conversion to the various products, calculated per mole of incoming 3-picoline as functions of temperature. The average of the mole ratios oxygen/3-picoline and steam/3-picoline was 42 and 82, respectively, and the space velocity was 2600 h^{-1} .

- × 3-Picoline (unconverted)
- Niacin
- △ 3-Pyridinealdehyde
- ◇ Carbon dioxide
- Carbon monoxide
- + Hydrogen cyanide

Figure 5

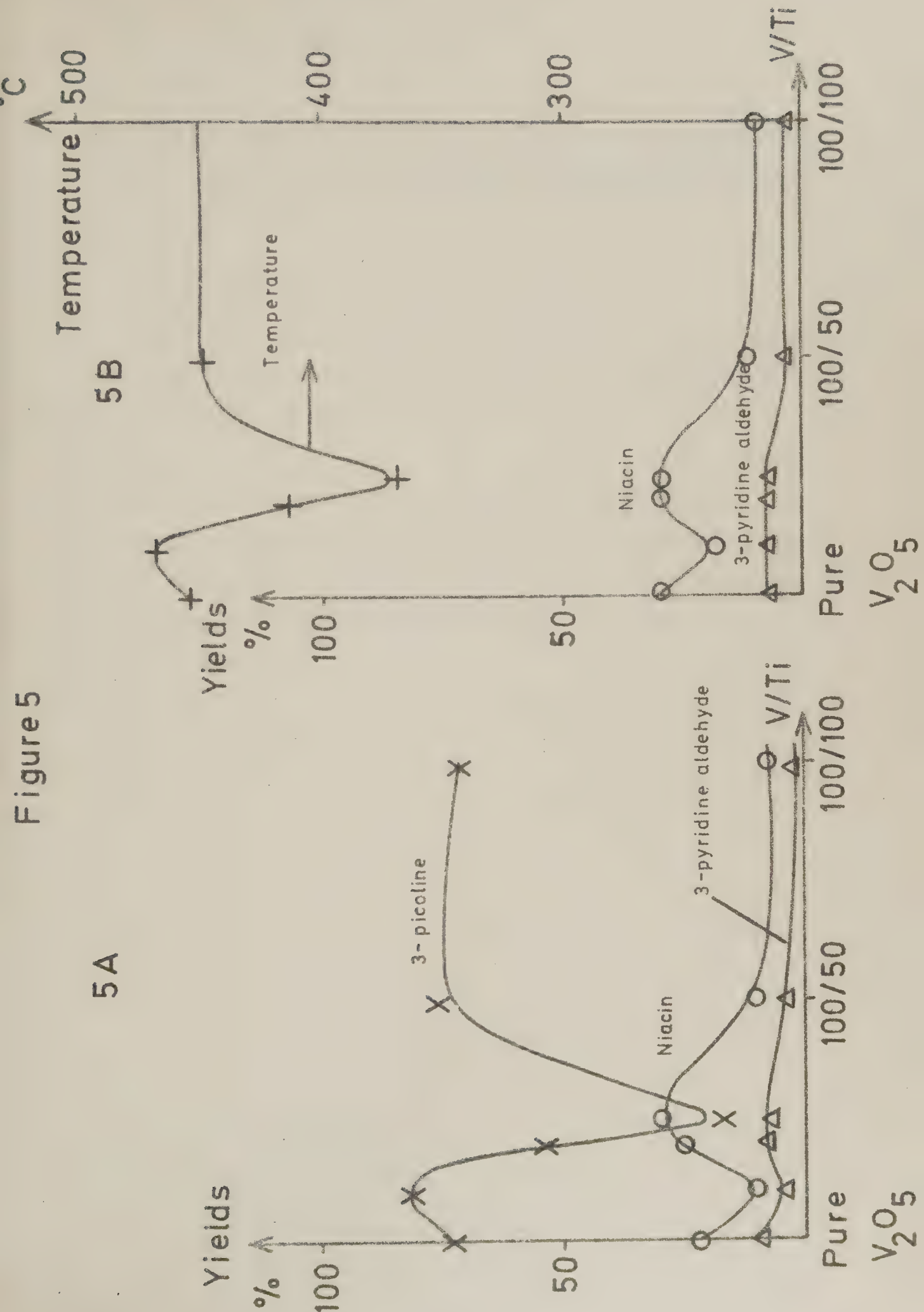


Figure 5. The effect of promotion with TiO_2 on vanadium oxide catalyst on the catalytic vapour phase oxidation of 3-picoline

- A. The mole percentage of unconverted 3-picoline and the conversion to niacin and 3-pyridinealdehyde calculated per mole of incoming 3-picoline at constant temperature, 375°C , as functions of the atom ratio V/Ti.
- B. The mole percentage of the conversion to niacin and 3-pyridinealdehyde, calculated per mole of incoming 3-picoline at the maximum yield of niacin and the corresponding temperature as functions of the atom ratio V/Ti.

PREPARATION OF PYRIDINEMONOCARBOXYLIC ACIDS BY CATALYTIC VAPOUR PHASE OXIDATION OF ALKYL PYRIDINES

Part II. Oxidation of 2-methyl-5-ethylpyridine to niacin

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Synopsis

The vapour phase air oxidation of 2-methyl-5-ethylpyridine (MEP) has been investigated, and the various oxidation products identified. Using a doubly promoted vanadium catalyst, V_2O_5 - TiO_2 - K_2O , a 98% (mole) conversion of MEP was obtained with a yield of 36% for niacin and 18% for recirculatable products (i.e. products with an intact 3-picoline skeleton) at a temperature of $413^\circ C$ and a space velocity of 5500 h^{-1} . In a comparison of the singly promoted catalysts, varying the atom ratio V/Ti, the catalyst V/Ti = 100/25 was found to be most active. In a comparison of different preparation temperatures for the same catalyst, $1250^\circ C$ was found to be most satisfactory. A reaction scheme is proposed with the corresponding rate constants and apparent activation energies.

1. Introduction

As mentioned in part I¹, 3-pyridinecarboxylic acid (nicotinic acid, niacin) is a technically valuable product. In the large scale preparation of niacin, 2-methyl-5-ethylpyridine (MEP) is usually the starting material in a liquid phase oxidation. The present investigation was undertaken in order to study the

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catalytic vapour phase air oxidation of MEP, bearing in mind the possibility of developing a large scale method of producing niacin.

Attempts have been made previously to oxidize MEP to niacin in the vapour phase using air as the oxidizing agent²⁻³. The only oxidation products mentioned in these references besides niacin are carbon dioxide and hydrogen cyanide.

Chekmareva et al.⁴ state that heating the catalyst mixture to 1200-1300°C during preparation results in the best yield of niacin from the oxidation of quinoline. With this in mind the catalysts used in the investigations below were normally melted at 1250°C.

For the oxidation of 3-picoline one reaction scheme has previously been proposed⁵. Below a reaction scheme for the oxidation of MEP is proposed based on the observed product distribution. The corresponding rate constants and apparent activation energies have been calculated. The primary aim of this reaction scheme is to aid in the design of a reactor, but certain mechanistic conclusions may also be drawn, as discussed below.

2. Experimental

2.1 Apparatus and procedure

The same apparatus and procedure as presented in part I¹ were used.

2.2 Analytical

The analytical methods were the same as for the oxidation of picoline presented in part I¹, to which the following must be added: The so-called tar products were estimated in most experiments by weighing the evaporated aqueous phase (normally 10 ml) in the acid analysis. In order to obtain this aqueous phase, two tubes with glass wool were washed, whereupon small amounts of glass wool were obtained as a contaminant which could not be removed by filtration. The amount of glass wool contamination varied somewhat from experiment to experiment, causing an uncertainty in the tar estimations. The average amount was estimated and the amount of tar in an experiment was calculated by subtracting this average plus the amount of acid from the estimated weight of the evaporated aqueous phase. The molecular weight of the tar was taken to be 150 (according to vapour phase osmometry, Hitachi Perkin-Elmer, 115).

2.3 Material

All chemicals used were of laboratory reagent purity.

2.4 Catalysts

1-17 Catalysts 1-17 were prepared by mixing the components and keeping them in the molten state at 1250°C in a porcelain crucible for 3 hours (catalysts 4, 12 and 14 however for only 1 hour). For the following procedure, see part I¹ (catalysts No 4-13).

The atom ratios for the components in the different catalysts are shown in table I.

18-20 Catalysts 18-20 were prepared as 1-17 above, except that the temperatures of melting were instead 700°C (No 18), 900°C (No 19), and 1100°C (No 20).

21-22 Catalysts 21-22 were prepared as 1-17 above, except that the temperature of melting was instead 900°C and the crucible was made of nickel. Catalyst 22 was poured in the molten state onto a nickel foil where it was allowed to cool.

The specific area of these catalysts (1-22) was 0.2 - 1.0 m²/g with no significant trend.

23-24 Since the experiments with 3-picoline according to part I¹ were performed, a new patent for the oxidation of 3-picoline has been published⁶. Catalyst 23 was prepared according to this patent, in which the components were sintered at 900°C as oxides in a nickel crucible. Catalyst 24 was prepared by precipitating the components on silicon carbide (carrier) followed by sintering at 700°C for 2 hours in a nickel crucible.

The particle size of the catalysts was 14-25 mesh.

3. Results and discussion

3.1 The oxidation products of MEP

Besides niacin several other products of the oxidation of MEP were obtained. These were identified by gas chromatography and

mass spectrometry. The following substances could be detected: 5-ethyl-2-pyridinealdehyde, 2-methyl-5-vinylpyridine, 3-ethylpyridine, 3-vinylpyridine, 3-pyridinealdehyde, niacin, pyridine, maleic acid, carbon dioxide, carbon oxide, water, and hydrogen cyanide. Furthermore a "tar product", which among other things probably consists of polymerisation products from vinylpyridines, was obtained. Isocinchomeronic acid, which is obtained as an intermediate in the liquid phase oxidation of MEP, is not obtained at all as a product at the vapour phase oxidation.

For each catalyst the conversion (def.: see part I¹) and product distribution were investigated as functions of the temperature. Normally experiments were carried out for each catalyst, at five to seven different temperatures at 25°C intervals. A typical product distribution is shown in figure 1. The percentage of 2-methyl-5-vinylpyridine is generally below 1% and 3-vinylpyridine somewhat higher. On the other hand, 5-ethyl-2-pyridinealdehyde and 3-ethylpyridine are formed in rather large amounts. The percentage of these intermediates go through maxima with increasing temperature. The percentage of 3-pyridinealdehyde is low, probably because it is rapidly oxidized to niacin and/or it is not an important intermediate for niacin. Furthermore, the percentage of pyridine does not normally exceed 3% at any temperature. As shown in part I¹, the thermal decarboxylation of niacin is only a few per cent under these process conditions.

At higher temperatures, smaller amounts of maleic acid are found due to the destruction of the pyridine ring. The total oxidation

products, carbon dioxide, carbon monoxide, and hydrogen cyanide, like the tar products, increase in yield with increasing temperature.

The percentage of niacin goes through a maximum with increasing temperature. The reason for the decrease in the percentage yield of niacin is largely dependent on the increasing extent of total oxidation. The decarboxylation to pyridine is, as mentioned earlier, of minor importance.

3.2 Conversions, yields and selectivities for the oxidation of MEP to niacin

In order to determine suitable test conditions for the different catalysts, the same catalyst ($V_2O_5/SnO_2 = 1/1.5$) as in the oxidation of 3-picoline¹ was used.

Experiments with this catalyst led to the choice of the following test conditions: space velocity 7000 h^{-1} , mole ratio oxygen/MEP = 75 and steam/MEP = 175. The catalyst bed volume was 5.5 cm^3 and the length was 23 mm. The maximum temperature variation in this bed was 12°C at 400°C . The maximum niacin yield for this catalyst was obtained at 3700 h^{-1} . However, in order to get a high catalyst productivity from a technical viewpoint a space velocity of 7000 h^{-1} was chosen for the test experiments.

In table I the percentage of the major products at maximum conversion to niacin are shown. The maximum niacin yield without recirculation is obtained at this maximum.

For the test conditions with catalyst V/Ti = 100/25 (No 5), 35% niacin was obtained. The second best value, 34%, was obtained for the pure vanadium oxide catalyst without promotor additives (No 1). On the average, the losses consist of about two thirds total oxidation products and one third tar products.

The possibility of increasing the yield of niacin by recirculation has been considered.

In the first case only unconverted MEP is recirculated, which was found to give no increase of the niacin yield. This is due to the fact that the maximum of selectivity and yield are obtained at the same temperature. The reason for this is that MEP is vigorously converted also at lower temperatures, when intermediates for niacin are primarily formed and not niacin itself.

In the second case, intermediates with an intact 3-picoline-skeleton are also recirculated, which led to an increase in the niacin yield. For catalyst No 5 above the maximum niacin yield was thus increased from 35% without recirculation to 44% with recirculation of both MEP and intermediates. The 44% yield was obtained at a 10°C lower temperature. The possibility of also recirculating the tar has not been considered.

3.3 Promotion of vanadium oxide by titanium oxide

3.3.1 The effect of the promotion on the oxidation of MEP

In figure 2 A the mole percentages of unconverted MEP and MEP converted to niacin at 400°C are plotted against different V/Ti atom ratios. It is clear from the figure that the largest extent of conversion of MEP and the best yield of niacin at 400°C are obtained at V/Ti = 100/25.

In figure 2 B, the maximum niacin yield and the temperature at this maximum are shown as functions of the V/Ti atom ratio. The catalyst with V/Ti = 100/25 is also shown to be most active by these data. At this atom ratio the maximum niacin yield is obtained at a 35°C lower temperature than that for the unpromoted vanadium oxide. This increase in the catalyst activity has been obtained with no significant decrease in the maximum conversion to niacin on a single pass in the reactor, i.e. the same effect by promoting with titanium oxide is in principle obtained for the oxidation of MEP as for the oxidation of 3-picoline¹. Thus a considerable increase in activity has been obtained with no appreciable decrease in maximum conversion to niacin and with no great decrease in selectivity.

3.3.2 The effect of the promotion on the catalyst

X-ray diffractograms have been recorded for all the unused catalysts prepared with different V/Ti atom ratios. No new phases could be determined, and only peaks from vanadium pentoxide and titanium dioxide (rutile) were detected. The same results have

been observed by Sterligova et al.⁷ and Piechotta et al.⁸ for the same system, although with somewhat different V/Ti ratios.

The unused and used catalysts were further analyzed with Electron Spectroscopy for Chemical Analysis (ESCA) in our laboratory. For all the catalysts used, a band widening of the vanadium peak ($V\ 2p_{3/2}$) could be detected. If vanadium occurs in more than one valence state in the catalyst, the $V\ 2p_{3/2}$ peak is wider than the peak from pure V_2O_5 . The oxidation state of the surface could thus be calculated by a linear approximation.

In all cases, the full width at half maximum (= FWHM) of $V\ 2p_{3/2}$ peak corresponded to an oxidation state around the vanadium oxide V_6O_{13} at the inlet of the catalyst bed, and the FWHM then decreased to about that of V^{5+} at the outlet. A corresponding colour change was also detected. The same variation of oxidation state has been described by Simard et al.⁹ for a vanadium oxide catalyst with no promotor additive. It must also be pointed out that this change in oxidation state of vanadium in our catalysts occurs only on the surface. If the catalyst is crushed, the FWHM of the V-peak corresponds to unused catalyst (V^{5+}).

In the oxidation of propene according to Colpaert¹⁰: "The results indicate that V_6O_{13} is involved in the catalytic process of selective oxidation."

Blanchard et al.¹¹ have examined the oxidation of butene with catalysts prepared from different mixtures of vanadium pentoxide and titanium dioxide. They examined the activation energy for

the heteromolecular isotope exchange of oxygen on the catalyst. They found that for a mixture of 35 mole percent titanium dioxide with vanadium pentoxide (corresponds to $V/Ti = 100/27$), this activation energy had a minimum.

In an examination of four different V/Ti ratios of the catalysts, Fabuss¹² found, that the reduction rate of V_2O_5 was greatest at 70% V_2O_5 and 30% TiO_2 for oxidation of naphthalene.

Colpaert et al.¹³ describe how inclusions of a different composition in a V_2O_5 lattice create local stress, which then can facilitate the formation of V_6O_{13} . Further they propose that an enhanced oxygen loss rate is obtained in the boundaries between V_2O_5 and V_6O_{13} .

The catalyst of pure vanadium oxide (No 1) and that with the atom ratio 100/25 (No 5) have been examined in our laboratory in an electron microscope with gas reaction attachment. When air was added at 400 - 500°C, crystal growth could be detected for both catalysts.

Catalyst $V/Ti = 100/25$ (No 5) has further been examined with Secondary Ion Mass Analysis. The distribution of titanium dioxide is shown in figure 3. From this analysis it is clear that the titanium dioxide exists mostly as separate aggregates, 0.5 - 5 microns, in the V-oxide phase. In connection with this it should be pointed out that a pure titanium dioxide catalyst yields almost no niacin at all ($< 2\%$) under typical conditions described above.

With the above in mind, one explanation for the enhanced activity for catalyst V/Ti = 100/25 (No 5) might be that titanium dioxide creates the local stress described, so that the formation and stabilization of V_6O_{13} is facilitated in the reduction-oxidation-process¹⁴ in which 3-picoline¹ or MEP is oxidized by the catalyst. For the catalyst with atom ratio 100/25 (No 5), the frequency of such local stress is greatest per catalyst unit.

3.4 The effect of the preparation temperature on the catalyst V/Ti = 100/25

In order to investigate the influence of preparation temperature for catalyst V/Ti = 100/25, catalysts with this atom ratio were prepared in the temperature range 700 - 1250°C. Higher temperatures could not be used because of adverse effects on the crucible.

In figure 4 A unconverted MEP, and conversion to niacin and carbon dioxide at 400°C are shown as functions of the preparation temperature of the catalyst. Figure 4 B shows the effect on maximum niacin yield and the temperature at which the maximum is obtained. A high temperature in the preparation of the catalyst thus has a positive effect on the activity as well as the selectivity.

The reason for this effect is assumed to lie in the phase combination between the vanadium oxide and titanium oxide. Silicon could be detected on the catalyst surface by means of ESCA-analysis of the catalyst. Silicon is probably present as SiO_2 . For the catalyst melted in a nickel crucible (No 21) instead

of a porcelain crucible (No 19) as was normally the case, a somewhat higher niacin yield was obtained. Nickel could also be detected on the catalyst surface by ESCA. Nickel is probably present as Ni_2O_3 . These experiments show that contamination from the crucible material may have an effect.

For a quenched catalyst (No 22), an increase of the niacin yield and a decrease of total oxidation were obtained compared to catalysts prepared by the usual cooling method (No 21).

One explanation for the phenomena described in this section might be that cooling from even higher temperatures causes an even greater frequency of the local stress mentioned earlier. Rapid cooling also often creates internal stresses.

3.5 Experiments with addition of K_2O or Na_2O

As mentioned earlier, the active phase in the catalysts based on vanadium pentoxide seems to be correlated to $\text{V}_6\text{O}_{13}^{9-10}$. The addition of an alkali oxide to vanadium pentoxide with subsequent heating led via the so-called reaction of Prandtl¹⁵ to the formation of alkali-metal vanadyl vanadates $\text{K}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$, in which the oxidation state of vanadium is lowered when alkali is added. The various percentages of the promotor additives in our laboratory are shown in table I.

As seen in table I, no significant effect is obtained by either the K_2O or the Na_2O additives on either the niacin or the carbon dioxide formation. The catalyst V/Ti/K = 100/25/1.5 gave however a higher percentage of recirculatable products. The reason that

this favourable effect failed to appear can be that the steam blocks or neutralises the effect. No specially pure product was obtained with Na_2O either, as was the case with 3-picoline¹.

3.6 Optimum of space velocity

The maximum yields of niacin, as presented in table I are, as mentioned above, produced at a fixed space velocity of 7000 h^{-1} . In order to obtain an optimum value for one more of the process parameters, experiments were performed at seven different levels of space velocity at three different temperature levels for one catalyst.

The double promoted vanadium oxide catalyst $\text{V/Ti/K} = 100/25/1.5$ (No 13) gave, besides good activity and a good yield of niacin, a higher percentage of recirculatable products than the simple promoted catalyst. This catalyst was chosen, and the product distribution determined at the temperatures 375, 413, and 450°C . The space velocities were varied from 1900 - 9600 h^{-1} (see table 2).

The maximum yields of niacin were 32, 36, and 32% at the following combinations of space velocity/temperature ($^\circ\text{C}$): 3000/375, 5500/413, and 7000/450, respectively. For a 36% conversion to niacin the following products were also obtained: total oxidation products (25%), recirculatable products (18%) and tar products ($\sim 20\%$). The conversion was 98%.

By changing space velocity at these three temperatures no significant increase of maximum yield was obtained. The product distribution was essentially the same for the three different temperatures.

3.7 Reaction scheme and rate constants for the vapour phase oxidation of MEP

Among other things, on the basis of the data presented in 3.6, a reaction scheme and corresponding rate constants were calculated. Isothermal conditions have been assumed in the calculations, although a small temperature profile exists, as mentioned above.

A vapour phase oxidation experiment without catalyst in the reactor at 400°C gave about 1% 5-ethyl-2-pyridinealdehyde and about 0.5% carbon dioxide as the only products besides MEP. Therefore, the catalytic oxidation of MEP can be regarded as a heterogenous phase reaction.

In order to study the mass transfer effects, two series of experiments were performed: one with a catalyst volume of 7.0 cm³ (space velocity 5400 h⁻¹) and one with 40% more catalyst and at the same time 40% more reactant flow (but constant mole ratios as above). The corresponding catalyst bed lengths were 29 mm and 43 mm, respectively. The conversion of MEP at 375°C was 86% in the smaller catalyst bed and 92% in the larger one. The selectivities were about the same for both the situations. In the light of these experiments and the fact that the catalyst particles are rather small, mass transfer effects may be said to be rather minor.

For the vapour phase oxidation of o-xylene to phthalic anhydride, it is assumed that the oxidation consists of several successive and parallel steps to the different oxidation products¹⁶. One

reaction scheme for oxidation of 3-picoline over a vanadium-molybdenum-phosphorus catalyst has been proposed earlier⁵.

With this in mind, different reaction schemes were proposed. The corresponding equations were tested on an analogue computer with different values of the parameters. The best agreement was given by the reaction scheme presented in figure 5.

The reaction course was described with differential equations of the first order (shown in figure 6), as a great air excess (oxygen excess) prevails¹⁷. The agreement between theory and experiment at different reaction times is seen in figure 7.

Due to the limited capacity of the analogue computer, pyridine, 3-pyridinealdehyde, and vinylpyridines, which were obtained in small amounts (a few per cent), were neglected in the scheme, but these compounds are of course intermediates.

The resulting rate constants and apparent activation energies are shown in table 3.

The significance of this reaction scheme might of course be questioned as the experimental data for one temperature are few and the fit to the individual points is not particularly good. But several points speak for this reaction scheme:

- 1) The accuracy of the analytical methods with condensation of products is about the same as the distribution of the points from the curves.

- 2) If both the oxidation pathways numbers 2 and 3 (corresponding to k_2 and k_3 in figure 5) are not taken into account, it is impossible to fit the data at any of the three temperatures.
- 3) The reaction scheme is adapted at three different temperature levels at the same time.
- 4) The reaction scheme is in accordance with the scheme for 3-picoline oxidation proposed by Leitis et al.⁵ in which they also suggested several parallel oxidation paths from 3-picoline.
- 5) The mechanistic implications are reasonable: The reaction scheme proposes that the oxidation starts with three different selective oxidation paths, with different relative ratios at the different temperatures. It might for example be that both ionic and radical mechanisms exist^{9,18-19}. This reaction scheme also suggests the possibility of more than one active form of oxygen^{18,20}.

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Table 1. Catalytic vapour phase oxidation of MEP:

Yields (mole %) at the maximum conversion to niacin on a single pass,
(the conversion to the different products resp., calculated per mole incoming MEP).

Catalyst	Temp $^{\circ}\text{C}$	Niacin %	CO_2 %	CO %	HCN %	Tar (1) products %	5-ethyl- 2-pyridine- aldehyde %	5-ethyl- pyridine %	5-vinyl- pyridine %	uncon- verted MEP %	unconverted MEP and recirculative %
1. Pure V_2O_5	465	34	13	3	12	xx (2)	-	-	-	3	8
2. V/Ti = 100/10	455	31	24	14	4	xx (2)	-	-	-	4	5
3. V/Ti = 100/15	455	32	23	11	3	xx (2)	-	-	-	-	13
4. V/Ti = 100/20 (1 h)	430	25	28	8	3	37	-	-	3	-	5
5. V/Ti = 100/25	430	35	22	3	3	18	-	4	11	-	15
6. V/Ti = 100/30	435	28	19	2	2	21	-	3	5	3	22
7. V/Ti = 100/40	445	31	22	1	3	25	-	2	2	3	13
8. V/Ti = 100/100	460	23	22	2	4	28	-	-	-	-	4
9. V/Ti = 50/100	485	15	15	5	-	40	-	6	-	6	15
10. Pure TiO_2 (3)	— (3)	42	—	—	—	—	—	—	—	—	—
11. V/Ti/K = 100/25/0.5	430	29	24	12	4	23	-	-	-	2	2
12. V/Ti/K = 100/20/1.15 (1 h)	455	31	26	11	6	29	-	3	-	4	8
13. V/Ti/K = 100/25/1.5	450	33	19	9	2	20	2	6	6	3	23
14. V/Ti/K = 100/20/2.3 (1 h)	433	30	25	12	3	26	-	-	2	-	9

Table 1 continued

Catalyst	Temp °C	Niacin %	CO ₂ %	CO %	HCN %	Tar (1) products %	5-ethyl- 2-pyridine- aldehyde %	5-ethyl- pyridine %	5-vinyl- pyridine %	uncon- verted MEP %	unconverted MEP and recirculative %
15. V/Ti/K = 100/25/4.0	440	33	19	9	2	30	-	4	7	-	14
16. V/Ti/Na = 100/25/0.5	435	25	27	12	-	29	-	-	-	-	7
17. V/Ti/Na = 100/25/1.0	430	25	25	11	3	32	-	-	2	2	12
18. V/Ti = 100/25 (700°C)	455	18	10	10	11	17	-	2	-	11	14
19. V/Ti = 100/25 (900°C)	428	25	22	12	-	24	-	4	-	2	6
20. V/Ti = 100/25 (1100°C)	418	25	20	8	-	26	-	4	-	12	29
21. V/Ti = 100/25 (900°C in Ni)	425	31	24	13	4	24	-	1	-	7	12
22. V/Ti = 100/25 (900°C Ni, outpoured)	423	34	20	8	4	26	3	2	3	6	14
23. V/Cr/Sb/Sn = 100/77/ 1.3/11.6 (Ni, 900°C)	425	32	26	11	5	21	-	1	-	-	4
24. As 23 (precipitated, Ni, 700°C)	425	32	24	6	4	16	3	4	7	25	41

(1) = An uncertainty of 20% of the presented figures (e.g. 30% ± 6%) exists in the analyses of the tar products.

(2) = An analysis of the tar products has not been carried out.

(3) = In the temperature interval 325 - 525°C only 1 - 2% niacin was obtained, therefore no maximum could be determined.

Figure 1

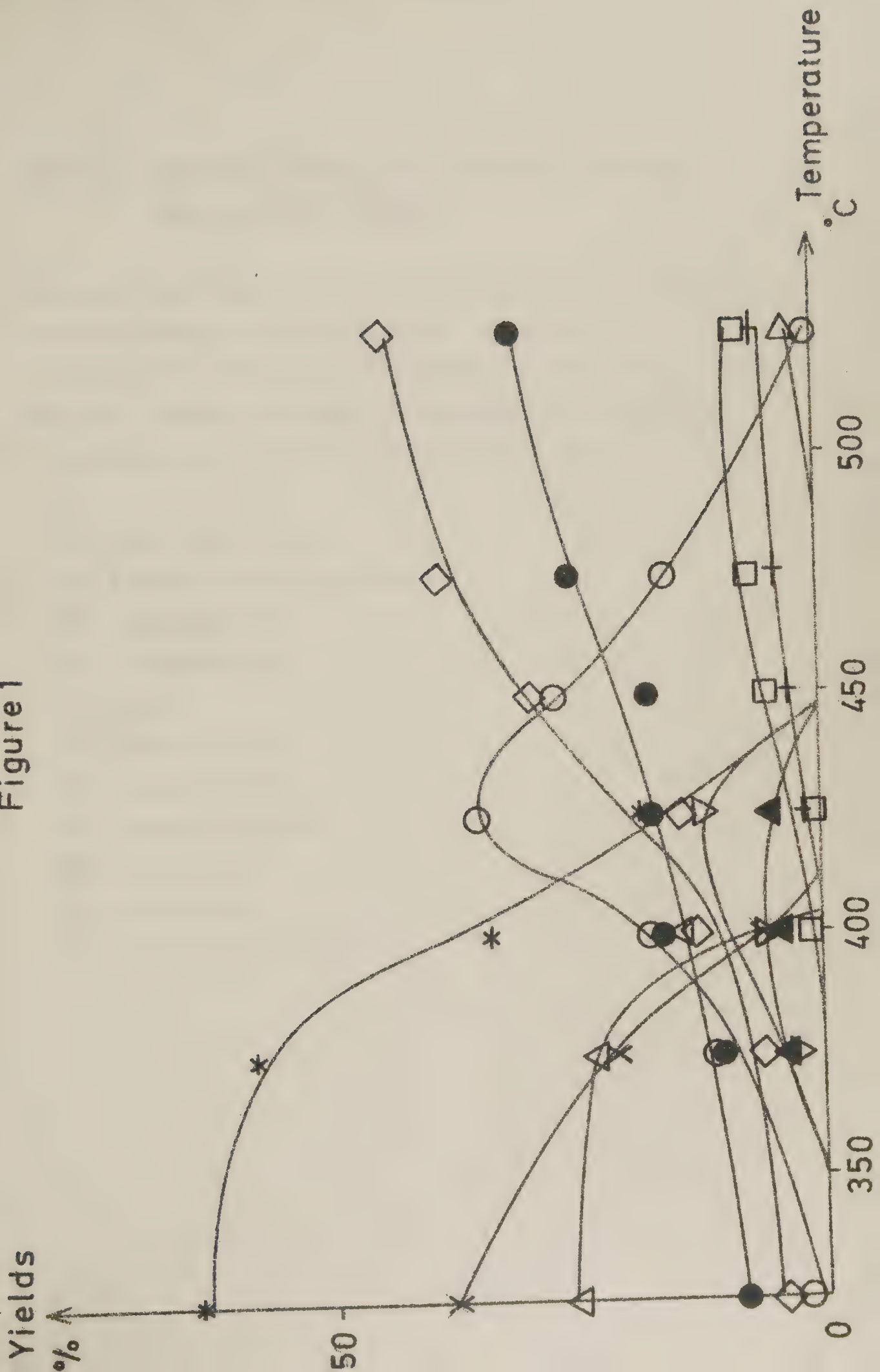


Figure 1. Catalytic vapour phase oxidation of MEP over
catalyst V/Ti = 100/25

The mole percentage of unconverted MEP and the conversion to the various products, calculated per mole of incoming MEP as functions of temperature. The average of the mole ratios oxygen/MEP and steam/MEP was 75 and 175, respectively, and the space velocity was $7\,000\text{ h}^{-1}$.

- × MEP (unconverted)
- △ 5-ethyl-2-pyridinealdehyde
- ▲ 3-ethylpyridine
- ▽ 3-vinylpyridine
- Niacin
- ◇ Carbon dioxide
- Carbon monoxide
- + Hydrogen cyanide
- Tar products
- ▷ Maleic acid
- * MEP and recirculatable

Figure 2

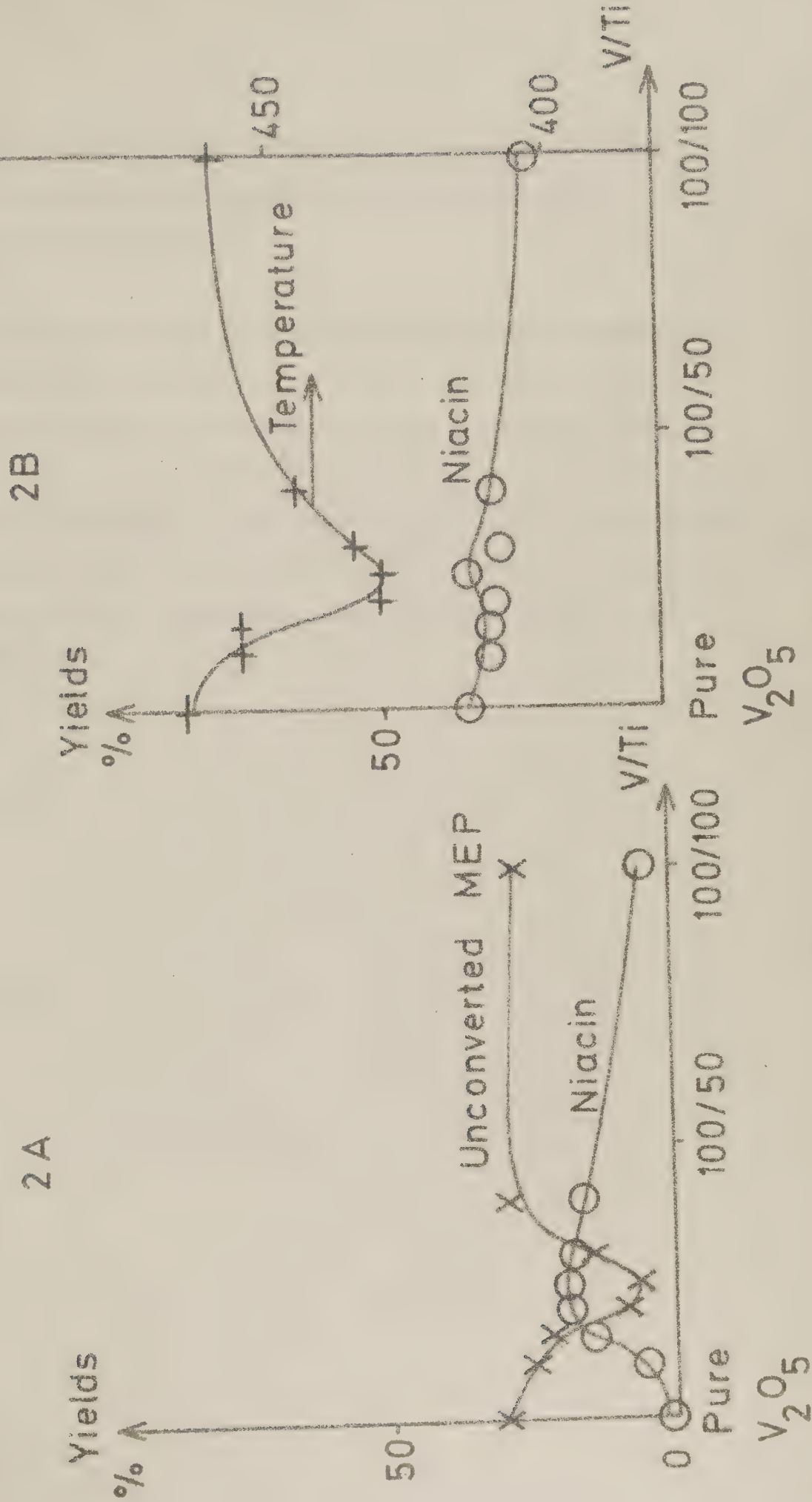


Figure 2. The influence of promotion with TiO_2 on vanadium
oxide catalyst on the catalytic vapour phase
oxidation of MEP

- A. The mole percentage of unconverted MEP and the conversion to niacin calculated per mole of incoming MEP at constant temperature 400°C as a function of the atom ratio V/Ti.
- B. The mole percentage of the conversion to niacin, calculated per mole of incoming MEP at the maximum yield of niacin and the corresponding temperature as a function of the V/Ti atom ratio.

Figure 3

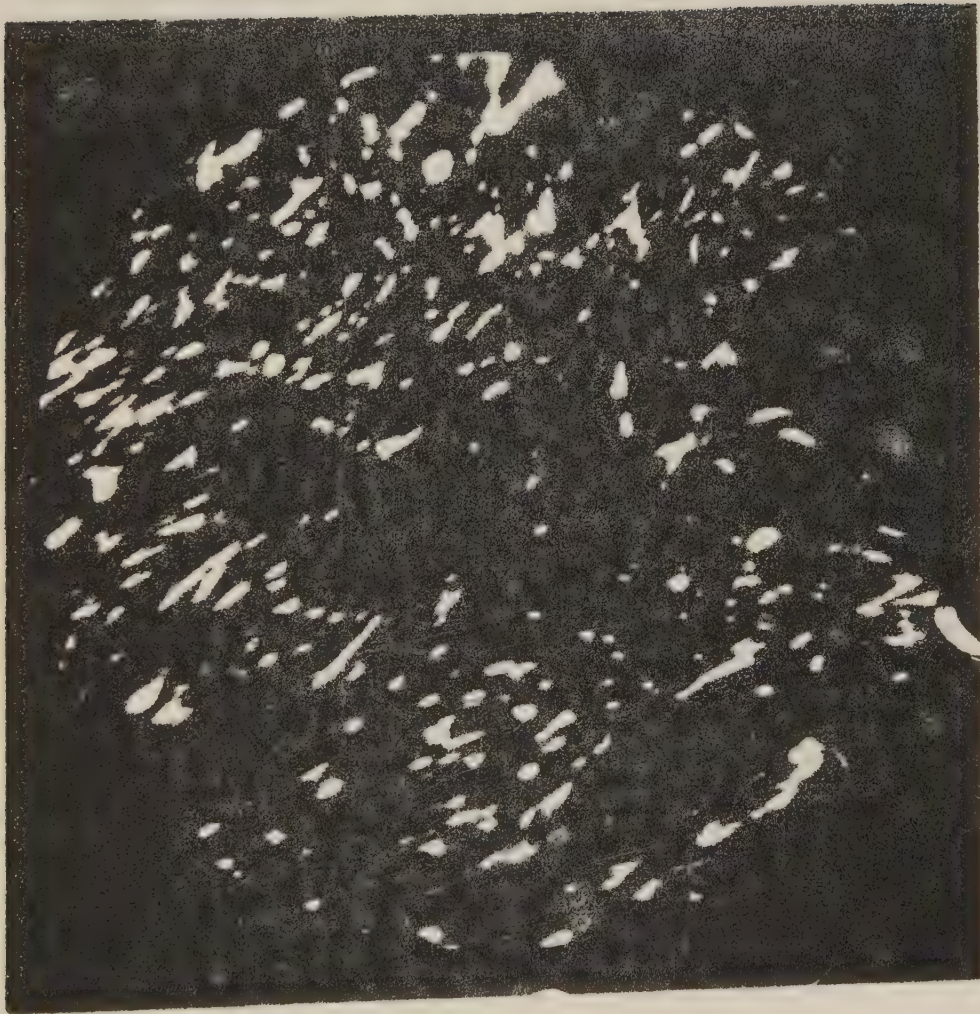


Figure 3. Secondary Ion Mass Analysis of catalyst V/Ti = 100/25

Photograph from Secondary Ion Mass Analysis showing a surface area with a diameter of 230 microns of the unused catalyst with atom ratio V/Ti = 100/25. The large black parts are probably nicks. The white parts correspond to titanium. Titanium is available mainly as small grains (0.5 - 5 microns) and as needle-shaped crystals (up to 15 microns). Where titanium is available dark shadows are seen on the vanadium picture.

Figure 4

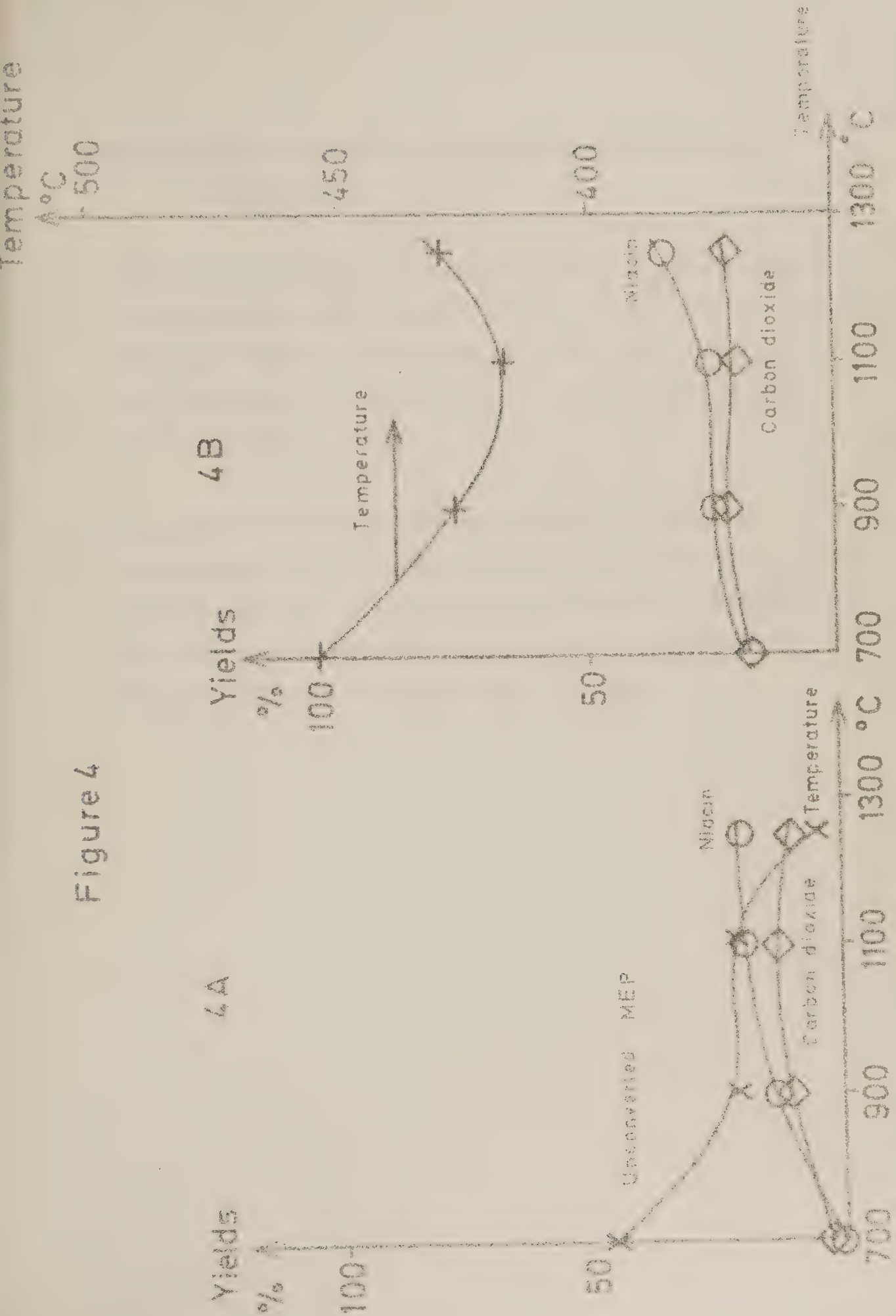


Figure 4. The effect of preparation temperature on the
catalyst V/Ti = 100/25

- A. The mole percentage of unconverted MEP and the conversion to niacin and carbon dioxide, calculated per mole of incoming MEP at a constant temperature of 400°C as functions of the temperature in the preparation of the catalyst with atom ratio $\text{V/Ti} = 100/25$.
- B. The mole percentage of the conversion to niacin and carbon dioxide, calculated per mole of incoming MEP at the maximum yield of niacin and the corresponding temperature as functions of the temperature in the preparation of the catalyst with atom ratio $\text{V/Ti} = 100/25$.

Table 2. The effect of space velocity on the yield of niacin

Yield (mole %) of niacin from the oxidation of MEP (catalyst No 13) as a function of space velocity and temperature. The average of the mole ratios oxygen/MEP and steam/MEP were 75 and 175 respectively.

Space velocity h^{-1}	% Yield of niacin at		
	375°C	413°C	450°C
9600	5	22	26
7000	8	19	32
5500	19	36	20
4500	26	30	16
3800	25	24	9
3000	32	18	4
1900	20	5	1

Figure 5. Reaction scheme for the catalytic oxidation of MEP

Reaction scheme for the catalytic oxidation of MEP.

A = MEP

B = 5-ethyl-2-pyridinealdehyde

C = 3-ethylpyridine

D = niacin

E = tar products

F = carbon dioxide + carbon monoxide + hydrogen cyanide

G = maleic acid

Figure 6. Differential equations for the catalytic oxidation
of MEP

The differential equations describing the reaction course of the oxidation of MEP shown in figure 5.

$$\frac{dC_A}{dt} = -k_1 \cdot C_A - k_2 \cdot C_A - k_3 \cdot C_A - k_{12} \cdot C_A$$

$$\frac{dC_B}{dt} = k_1 \cdot C_A - k_4 \cdot C_B - k_6 \cdot C_B - k_7 \cdot C_B$$

$$\frac{dC_C}{dt} = k_4 \cdot C_B + k_2 \cdot C_A - k_5 \cdot C_C - k_8 \cdot C_C - k_9 \cdot C_C$$

$$\frac{dC_D}{dt} = k_3 \cdot C_A + k_5 \cdot C_C - k_{10} \cdot C_D - k_{11} \cdot C_D$$

$$\frac{dC_E}{dt} = k_6 \cdot C_B + k_8 \cdot C_C$$

$$\frac{dC_F}{dt} = k_7 \cdot C_B + k_9 \cdot C_C + k_{10} \cdot C_D + k_{12} \cdot C_A + k_{13} \cdot C_G$$

$$\frac{dC_G}{dt} = k_{11} \cdot C_D - k_{13} \cdot C_G$$

Figure 7

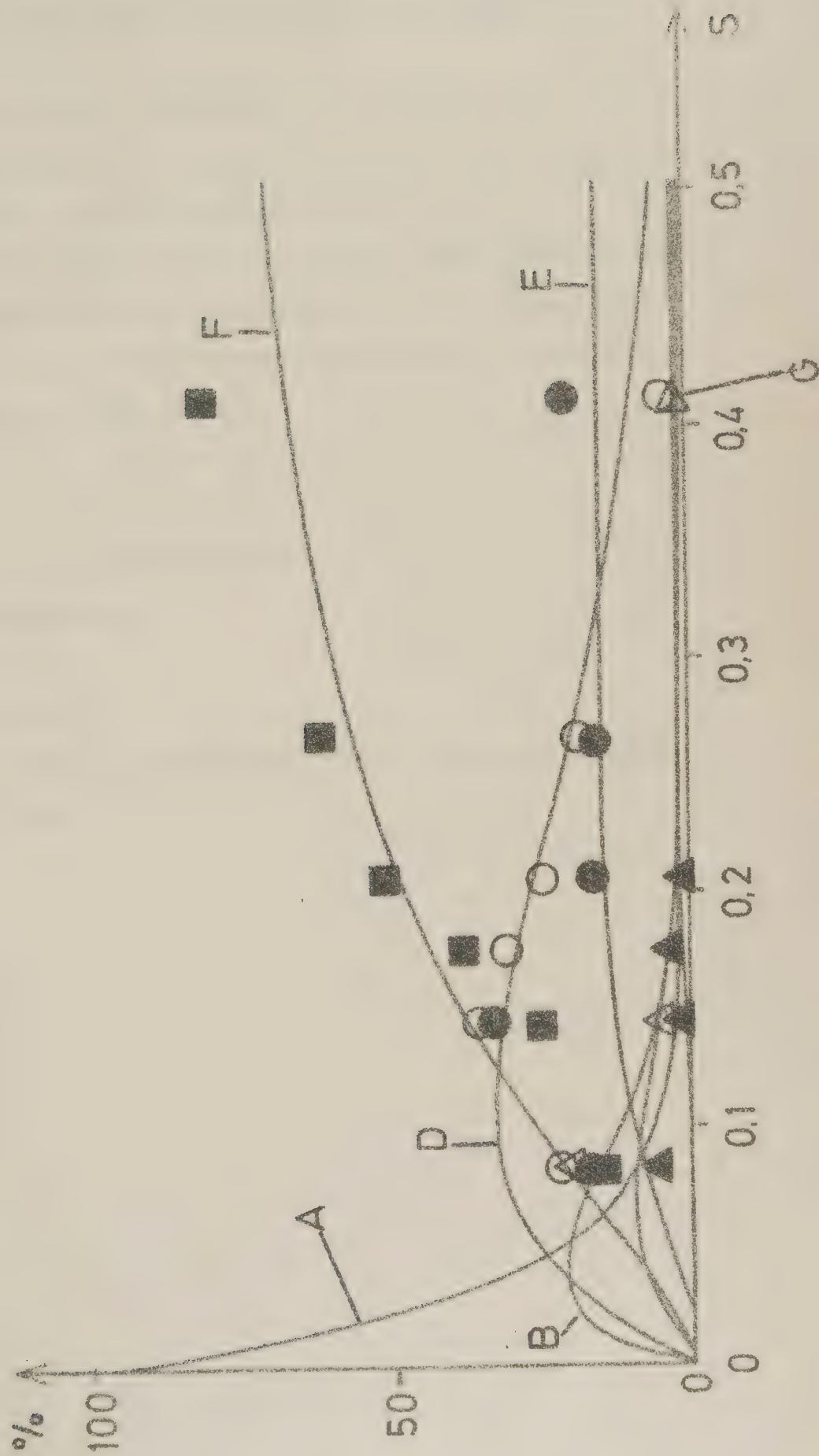


Figure 7. Catalytic vapour phase oxidation of MEP

The mole percentage of unconverted MEP and the conversion to the various products, calculated per mole of incoming MEP as functions of reaction time at 413°C .

The average of the mole ratios oxygen/MEP and steam/MEP was 75 and 175 respectively. The graphs are drawn by analogue computer, using the proposed reaction scheme (fig. 5) and the rate constants from table 2.

× A = MEP

△ B = 5-ethyl-2-pyridinealdehyde

▲ C = 3-ethylpyridine

○ D = Niacin

● E = Tar products

■ F = Carbon dioxide + carbon monoxide + hydrogen cyanide

▷ G = Maleic acid

Table 3. Rate constants and apparent activation energies
for the catalytic oxidation of MEP

The rate constants and apparent activation energies for the catalytic vapour phase oxidation of MEP at 375-450°C and low percentage of MEP (about 0.3% of total flow) over a catalyst of V_2O_5 - TiO_2 - K_2O (atom ratio V/Ti/K = 100/25/1.5).

Reaction number	Rate constants			Apparent activation energies kJ/mole
	375°C s ⁻¹	413°C s ⁻¹	450°C s ⁻¹	
1	13.6	15.5	16.8	11
2	0.2	1.0	8.8	210
3	2.9	8.4	17.5	95
4	13.3	18.2	19.6	20
5	16.1	18.7	19.9	11
6	0.2	1.8	16.2	240
7	0.1	1.4	12.0	230
8	5.6	7.7	10.5	33
9	5.9	8.0	11.5	35
10	3.9	4.9	4.5	7
11	0.2	0.4	2.4	140
12	0.2	1.2	7.2	200
13	1.0	2.0	8.1	110

